Supporting information for

Achieving efficient Tb^{3+} dual-mode luminescence via the Gd-sublattice-mediated energy migration in $NaGdF_4$ core-shell nanoarchitecture

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Experimental section

Reagents. All of the chemical reagents used in this experiment are analytical grade and were received without further purification. $GdCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.99%), $TmCl_3 \cdot 6H_2O$ (99.995%), $CeCl_3 \cdot 6H_2O$ (99.99%) and $TbCl_3 \cdot 6H_2O$ (99.99%) were purchased from Beijing Founde Star Science & Technology Co., Ltd. NaOH (98%), NH_4F (98%), methanol (99.5%), and ethanol (99.7%) were provided by Sinopharm Chemical Reagent Co., Ltd. Oleic acid (OA, 90%), 1-octadecene (ODE, 90%) were received from Aladdin Reagent Company.

Synthesis of $NaGdF_4$:Yb/Tm core nanoparticles. In a typical experiment, $GdCl_3 \cdot 6H_2O$ (0.5576g, 1.5 mmol), $YbCl_3 \cdot 6H_2O$ (0.5697g, 1.47 mmol), $TmCl_3 \cdot 6H_2O$ (0.0115g, 0.03 mmol) were taken in a 100 mL 3-necked flask at room temperature, and 30 mL of ODE along with 30 mL of OA was added. The resulting mixture was then heated to 160 ^oC under a N_2 atmosphere and held at this temperature for 15 min to get a homogeneous solution. Subsequently, the flake was cooled down to 60 ^oC, and 20 mL methanol solution containing NH_4F (0.463 g, 12 mmol), NaOH (0.300 g, 7.5 mmol) was added dropwise and stirred at 60 ^oC for 30 min to ensure that all fluoride was consumed completely. The reaction temperature was then increased to 100 ^oC to remove the methanol from the reaction mixture. Upon removal of methanol, the solution was heated to 310 ^oC and maintained at this temperature under a nitrogen flow for 60 min, at which time the mixture was cooled down to room temperature. The resulting nanoparticles were precipitated out through an addition of ethanol (20 mL), collected by centrifugation at 10000 rpm for 10 min, washed with ethanol three times, and finally dried at 60 ^oC in vacuum for 12 h.

Synthesis of $NaGdF_4$:Yb/Tm@$NaGdF_4$:Ce/Tb core-shell nanoparticles. For synthesis of

core/shell structure, $GdCl_3 \cdot 6H_2O$ (0.2732 g, 0.735 mmol), $CeCl_3 \cdot 6H_2O$ (0.0587g, 0.1575 mmol), and $TbCl_3 \cdot 6H_2O$ (0.0588g, 0.1575 mmol) were added to the mixture of 6 mL OA and 15 mL ODE in a three-necked flask (100 mL) at room temperature. Then, the slurry was heated to 160 °C under a N_2 atmosphere with vigorous magnetic stirring for 15 min to form an optically transparent solution. After the mixture was cooled down to 60 °C, the as-prepared core nanoparticles (0.2124 g) in 4 mL cyclohexane were added along with a 10 mL methanol solution of NH_4F (0.170 g, 4.4 mmol) and NaOH (0.0115 g, 2.75 mmol). The resulting mixture was stirred at 60 °C for 30 min, at which time the reaction temperature was increased to 100 °C to remove the cyclohexane and methanol. Then the solution was heated at 310 °C under a nitrogen flow for 60 min and cooled down to room temperature. The resulting core-shell nanoparticles were precipitated out by the addition of ethanol, collected by centrifugation, washed with ethanol three times and finally dried at 60 °C in vacuum for 12 h.

Characterization. Powder X-ray diffraction (XRD) measurements were performed on an AXS D8 advance diffractometer at a scanning rate of 10 °/min in the 2θ range from 10° to 80° with Cu Kα radiation (λ=0.15406 nm). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) patterns were recorded on JEM-200CX with a field emission gun operating at 200 kV. Images were acquired digitally on a Gatan multiple CCD camera. UC emission spectra were recorded with a Jobinyvon FL3-221 fluorescence spectrophotometer equipped with a 980 nm laser diode Module (K98SA3M-54W, China) as the excitation source. All the measurements were performed at room temperature.

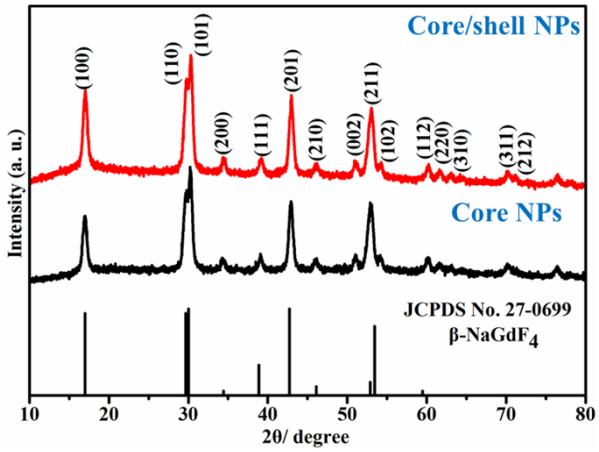

Fig. S1 The XRD patterns for $NaGdF_4$:49%Yb^{3+}/1%Tm^{3+} core NPs , and $NaGdF_4$:49%Yb^{3+}/1%Tm^{3+}@$NaGdF_4$:15%Ce^{3+}/15%Tb^{3+} core-shell NPs. The standard data for hexagonal $NaGdF_4$ (JCPDS No. 27-0699) is shown as a reference.

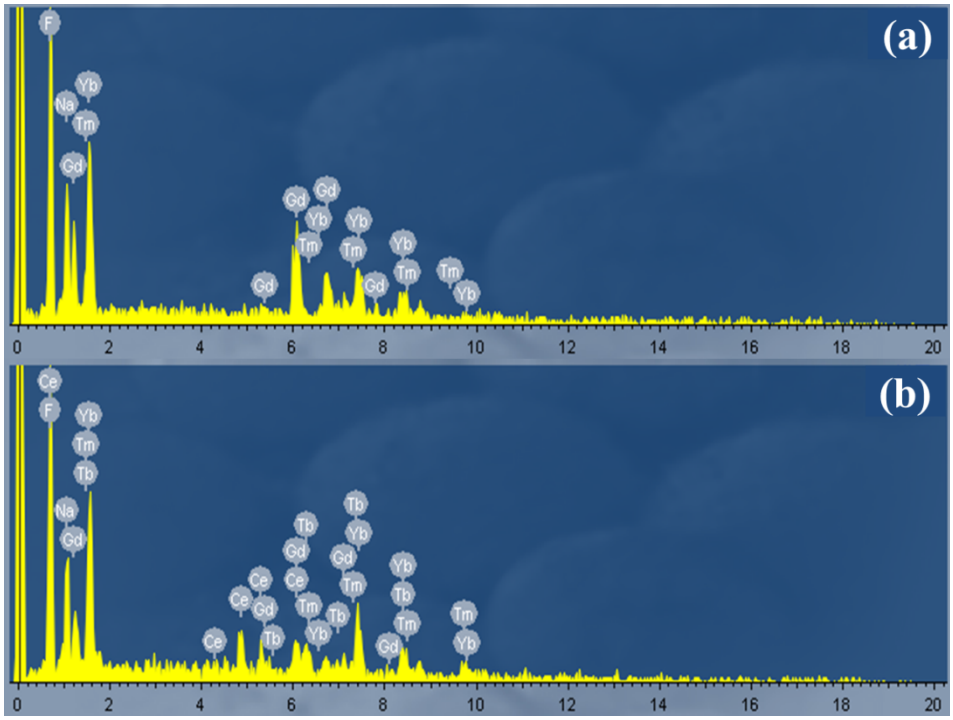

Fig. S2 The energy-dispersive X-ray spectroscopy analyses of (a) $NaGdF_4:Yb^{3+}/Tm^{3+}$ core NPs and (b) $NaGdF_4:Yb^{3+}/Tm^{3+}@NaGdF_4:Ce^{3+}/Tb^{3+}$ core-shell NPs, revealing the presence of the doped elements of Yb, Tm for core NPs and Yb, Tm, Ce and Tb for core-shell NPs.

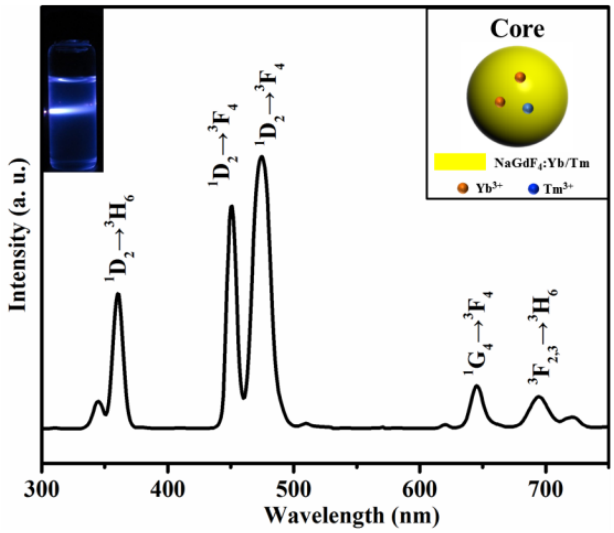

Fig. S3 UC emission of $NaGdF_4:49\%Yb^{3+}/1\%Tm^{3+}$ core NPs under the excitation of a 980 nm continuous wave (CW) diode laser at a power density of 10 W/cm^2. The emission spectra were obtained in cyclohexane solutions comprising 1 wt% NPs under 980 nm laser diode excitation.

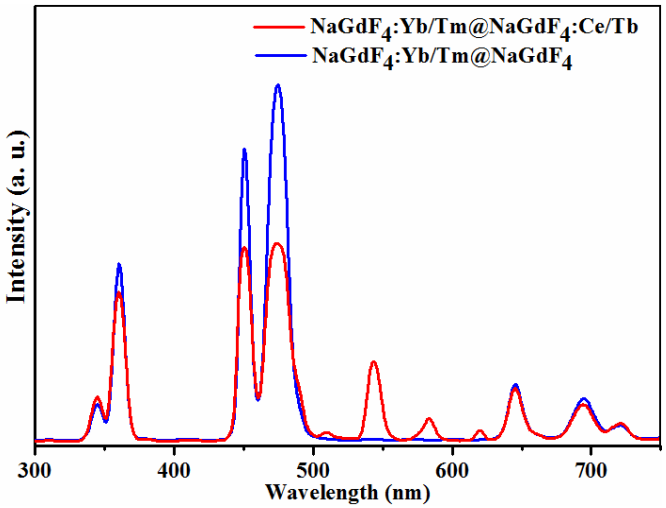

Fig. S4 UC emission spectra of $NaGdF_4$:49%Yb^{3+}/1%Tm^{3+}@$NaGdF_4$:15%Ce^{3+}/15%Tb^{3+} and NaGdF4:49%Yb^{3+}/1%Tm^{3+}@$NaGdF_4$ core-shell NPs.

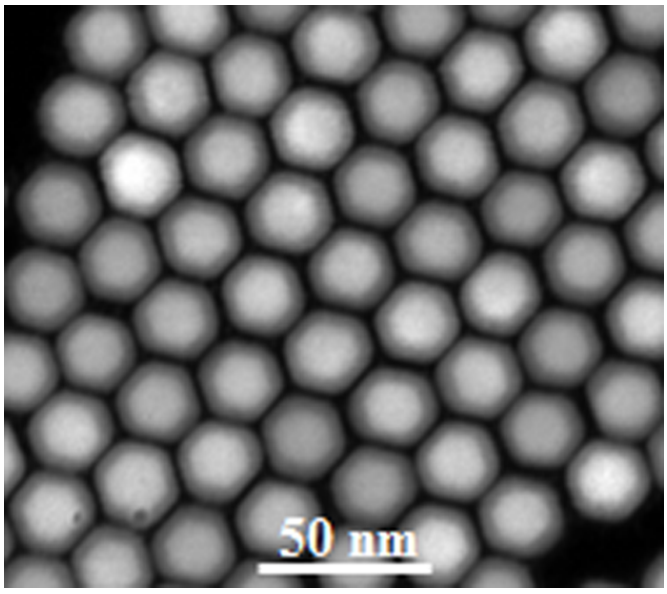

Fig. S5 STEM-HADDF image of $NaGdF_4$:Yb^{3+}/Tm^{3+}@$NaYF_4$:Ce^{3+}/Tb^{3+} core-shell nanoparticles.

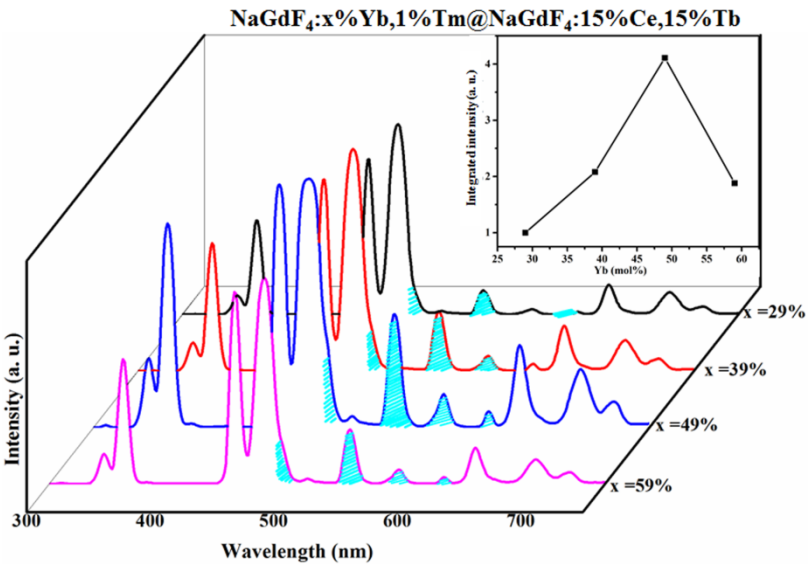

Fig. S6 EMU emission spectra for a series of $NaGdF_4$:x%Yb^{3+}/1%Tm^{3+}@$NaGdF_4$:15%Ce^{3+}/15%Tb^{3+} core-shell NPs as a function of different dopant concentrations of Yb^{3+} ions (x = 29, 39, 49, 59). The emission spectra were obtained in cyclohexane solutions comprising 1 wt% NPs under 980 nm laser diode excitation.

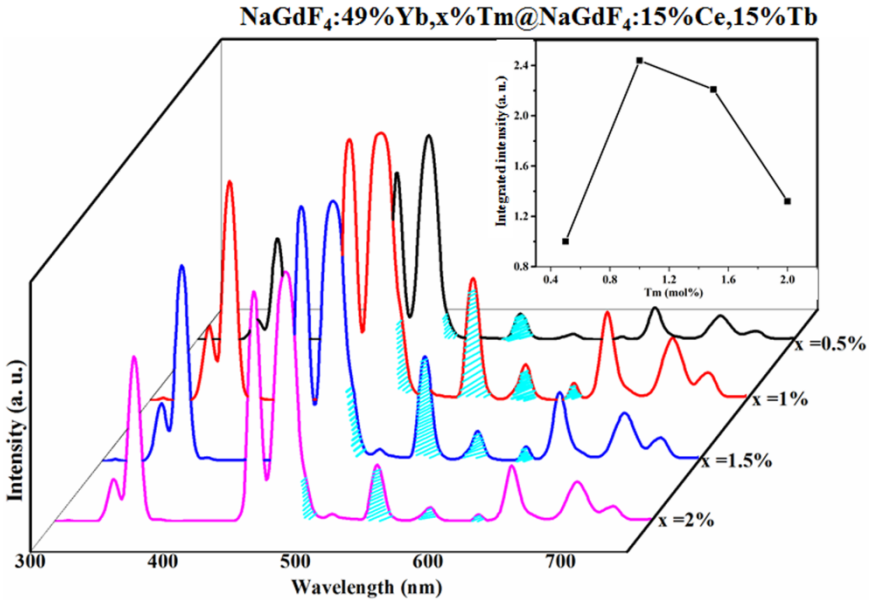

Fig. S7 EMU emission spectra for a series of $NaGdF_4$:49%Yb^{3+}/x%Tm^{3+}@$NaGdF_4$:15%Ce^{3+}/15%Tb^{3+} core-shell NPs as a function of different dopant concentrations of Tm^{3+} (x=0.5, 1, 1.5, 2). The emission spectra were obtained in cyclohexane solutions comprising 1 wt% NPs under 980 nm laser diode excitation.

As we known, the dopant concentration of lanthanide ions has a great impact on luminescence properties via tuning the average distance between neighboring dopant ions[1, 2]. Thus, a series of $NaGdF_4$:Yb^{3+}/Tm^{3+}@$NaGdF_4$:Ce^{3+}/Tm^{3+} core-shell NPs were synthesized in order to optimize doping concentration of the Yb^{3+}/Tm^{3+} ion pair for efficient EMU process. In our experiments, the core was doped with various concentrations of Yb^{3+} and Tm^{3+} ions, while the dopant concentrations

of Tb^{3+} and Ce^{3+} in the shell were fixed to be 15 and 15 mol%, respectively. By comparing the emission intensity of Tb^{3+}, we found that the optimum dopant concentration of Yb^{3+} and Tm^{3+} for achieving maximum Tb^{3+} emission were 49, 1 mol%, respectively (Fig. S6 and Fig. S7). To optimize dopant concentrations of Ce^{3+} and Tb^{3+} ions for achieving efficient DC process, we also synthesized a series of $NaGdF_4$:Yb^{3+}/Tm^{3+}@$NaGdF_4$:Ce^{3+}/Tm^{3+} core-shell NPs with different dopant concentrations of Ce^{3+} and Tb^{3+} in shell layer. From the photoluminescence data of the as-synthesized samples, the optimum concentrations of Ce^{3+} and Tb^{3+} for efficient DC emission under 254 nm excitation is estimated to be 15 and 15 mol%, respectively (Fig. S10 and Fig S11).

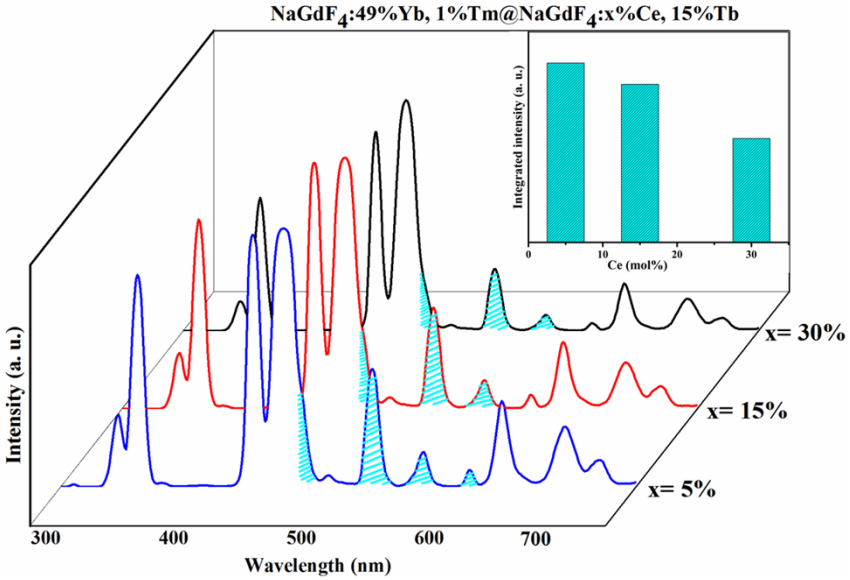

Fig. S8 EMU emission spectra for a series of $NaGdF_4$:49%Yb^{3+}/1%Tm^{3+}@$NaGdF_4$:x%Ce^{3+}/15%Tb^{3+} core-shell NPs as a function of different dopant concentrations of Ce^{3+} (5-30 mol%).

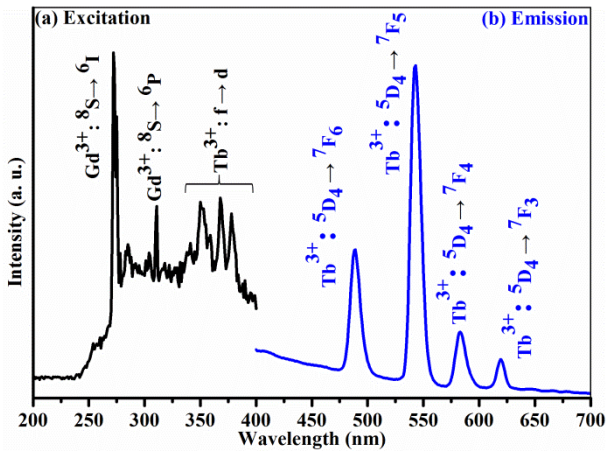

Fig. S9 (a) PL excitation (λ_{em} = 543 nm) and (b) DC emission (λ_{ex} = 275 nm) spectra for Tb^{3+} in $NaGdF_4$:Yb^{3+}/Tm^{3+}@$NaYF_4$:**Tb^{3+}** core-shell NPs.

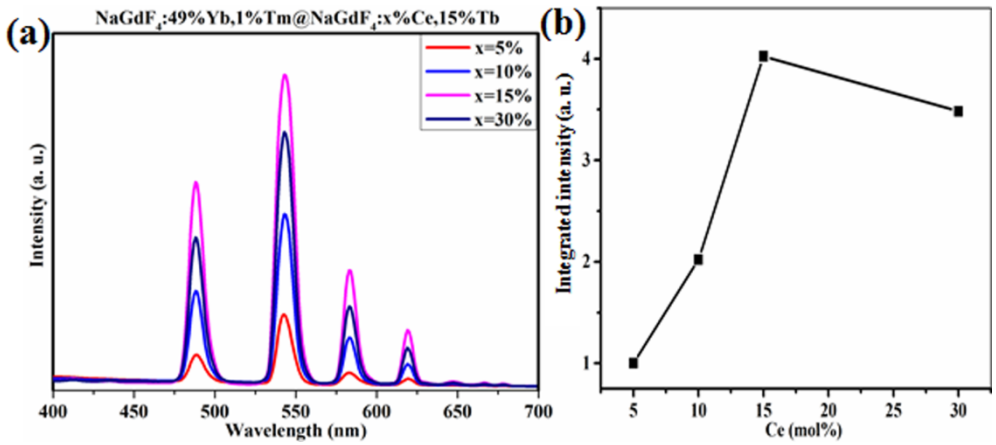

Fig. S10 DC emission spectra (λ_{ex} = 254 nm) for the as-obtained $NaGdF_4$:49%Yb^{3+}/1%Tm^{3+} @$NaGdF_4$:x%Ce^{3+}/15%Tb^{3+} core-shell NPs as a function of different dopant concentrations of Ce^{3+} (5-30 mol%).

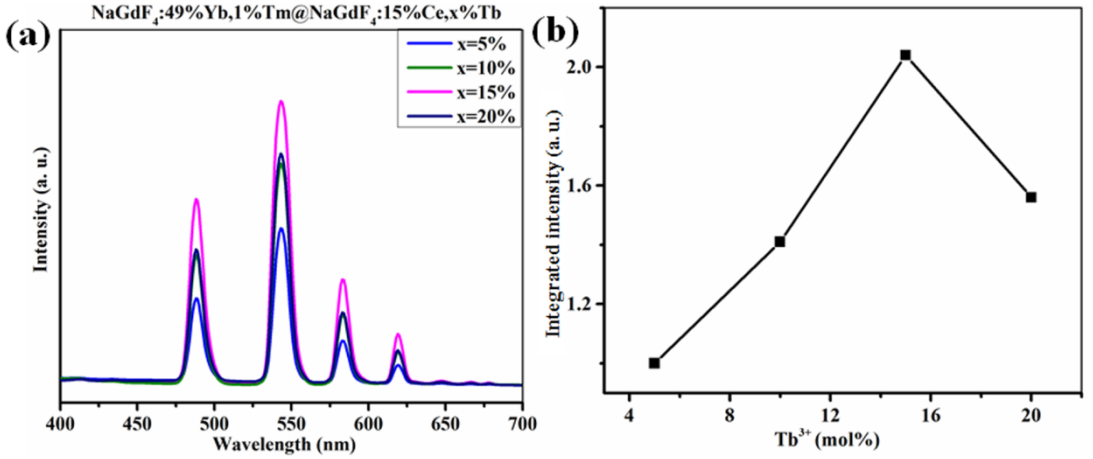

Fig. S11 DC emission spectra (λ_{ex} = 254 nm) for the as-obtained $NaGdF_4$:49%Yb^{3+}/1%Tm^{3+} @$NaGdF_4$:15%Ce^{3+}/x%Tb^{3+} core-shell NPs as a function of different dopant concentrations of Tb^{3+} (5-20 mol%).

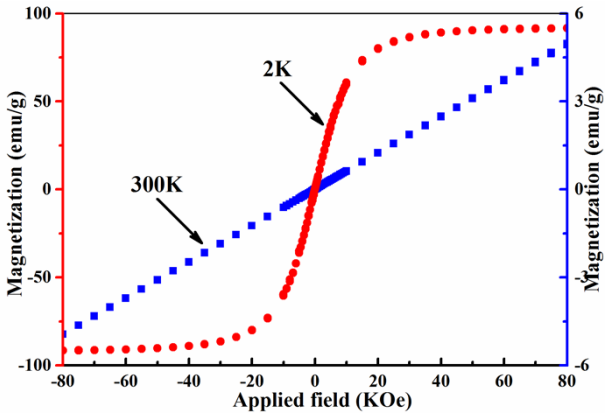

Fig. S12 Magnetization as a function of applied field for $NaGdF_4$:Yb^{3+}/Tm^{3+}@$NaGdF_4$:Ce^{3+}/Tb^{3+} core-shell NPs at 2 K and 300K.

Apart from efficient UC and DC luminescence, $NaGdF_4$:Yb/Tm@$NaGdF_4$:Ce/Tb core-shell NPs also exhibit paramagnetism at room temperature, originating from the intrinsic magnetic moment of Gd^{3+} with non-interacting and localized nature[3-5]. As shown in Fig. S12, the

magnetization of the core-shell nanocrystals at 20 KOe is around 1.5 emu/g, which is close to the reported value of the NPs used for common bio-separation. At low temperature (2 K), these core-shell NPs exhibit superparamagnetism with a saturation magnetization value of 90 emu/g. Hopefully, $NaGdF_4$:Yb/Tm@$NaGdF_4$:Ce/Tb core-shell NPs with dual-mode luminescence and proper parmagnetism are ideal for bio-labeling and magnetic resonance imaging applications in the further, after appropriate surface modifications.

References

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